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REFRACTORY ALLOYS

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STRUCTURE AND PHASE COMPOSITION OF COMPLEX REFRACTORY COATING AND OF THE REACTION ZONE OF INTERACTION WITH SINGLE-CRYSTAL ALLOY ZhS36-VI AFTER HIGH-TEMPERATURE HOLDS

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A complex coating consisting of three layers, i.e., a gas-circulation coating and a two-layer ion-plasma coating with an internal Ni – Cr – Al – Ta – Re – Y layer and an external Al – Ni – Cr – Y layer for protecting single crystal turbine rotor blades from high-temperature oxidation is considered. The fine structure and the phase composition of the complex coating and of the reaction zone of interaction with single-crystal alloy ZhS36-VI after high-temperature holds in a range of 1050 – 1300°C for 1 – 1000 h are studied.

Key words: single-crystal refractory nickel alloy, refractory coatings, secondary reaction zone, structure, phase composition, tcp phases.

INTRODUCTION

Modern single-crystal refractory nickel alloys with W, Ta, Re and Ru additives possess a high long-term strength but are oxidized intensely under the action of high temperatures. This makes it necessary to develop refractory coatings and technologies for long-term protection of high-pressure turbine rotor blades of aircraft gas turbine engines from refractory nickel alloys from oxidation at a temperature of up to 1150 – 1200°C [1, 2]. We have developed a complex diffusion-condensation protective coating with gradient distribution of alloying elements over the thickness for single-crystal rotor blades from alloy ZhS36-VI for advanced gas turbine engines [3].

It is known that an aluminide coat deposited between an ultimately alloyed single-crystal refractory nickel alloy and a coating produces a secondary reaction zone (SRZ) due to redistribution of the alloying elements [4 – 6]. This zone is represented by a $\gamma + \gamma'$ structure with segregations of tcp phases. The appearance of a SRZ is promoted by segregation inhomogeneity of single crystals with a high content of refractory elements (Re, W, Ta, Ru). This zone can appear due to deposition of an aluminide coating and due to a high-temperature hold of the coated alloy. A long-term high-temperature hold gives rise to phase transformations in this zone.

The aim of the present work was to continue the study of the structure and phase stability and of the composition of the arising phases and to identify them in a complex gradient CrAl GCC + Ni – Cr – Al – Ta – Re – Y IPC + Al – Ni – Cr – Y IPC coating and in the reaction zone of the interaction with single-crystal alloy ZhS36-VI under long-term high-temperature holds.

METHODS OF STUDY

We studied castings of single-crystal alloy ZhS36-VI with crystallographic orientation [001] obtained in commercial facilities of type UVNK-8P without liquid-metal coolant at a rate of crystallization of 3 mm/min. The average chemical composition of alloy ZhS36-VI [7] in wt.% is as follows: 4.0 Cr, 9.0 Co, 1.2 Mo, 11.7 W, 2.0 Re, 1.1 Ti, 1.1 Nb, 5.8 Al, the remainder Ni. The castings were subjected to a standard heat treatment that consisted of quenching, which included a homogenizing hold at 1310 ± 10°C for 4 h and cooling at a high rate (≥ 100 K/min), and two-stage aging at 1030 ± 10°C and 870 ± 10°C.

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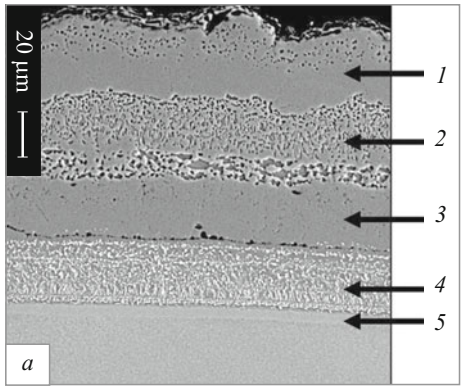


b

Layer*	Content of elements in the layer,** wt.%								
	Al	Ti	Cr	Co	Mo	W	Re	Ta	Other
1	20.5	–	6.5	0.9	–	–	0.2	0.9	–
2	19.5	–	13.5	1.7	–	–	0.5	1.0	0.2Y
3	19.5	0.5	7.0	3.3	–	–	–	0.7	0.2Y
4	14.5	0.5	7.0	3.8	1.1	20.0	3.1	–	0.5Nb
5	9.5	1.5	3.5	6.0	1.2	9.5	1.0	–	1.9Nb

* See Fig. 1a.

** The remainder nickel.

Fig. 1. Microstructure (*a*) and chemical composition (*b*) of the layers of a complex gradient coating on alloy ZhS36-VI [001] in the initial state: *1*) VSDP18 IPC (NiAl β-phase); *2*) Ni – Cr – Al – Ta – Re – Y IPC (a mixture of β-, γ-, and γ′-phases); *3*) NiAl β-phase of CrAl GCC; *4*) diffusion zone of CrAl GCC; *5*) a layer of γ′-phase between the alloy and the CrAl GCC.

The alloy was covered with a gas-circulation coating (GCC) of CrAl in a ShGA-1 device at 1000°C for 6 – 8 h at an excess pressure of 1.3 MPa of the gas atmosphere [8]. Then we performed diffusion annealing in vacuum at 1050°C for 2 h. After this a two-layer ion-plasma coating (IPC) was deposited on the GCC in a MAP-1 facility for ion-plasma deposition at a vacuum arc current of 500 – 700 A and electrical potential of the substrate of 5 – 10 V in vacuum no worse than 10^{-2} Pa [9].

The first layer of the IPC deposited on the CrAl GCC sublayer had the following chemical composition (in wt.%): 16.0 Cr, 11.0 Al, 1.5 Ta, 0.8 Re, 0.45 Y, the matrix Ni. The thickness of the layer was about 60 μm. Then we deposited a VSDP-18 (SL) second layer containing (in wt.%): 5.0 Ni, 5.0 Cr, 5.0 Y, the matrix Al. The complex gradient coating was subjected to diffusion annealing in vacuum at 1050°C for 3 h.

The specimens of alloy ZhS36-VI with a complex protective coating were subjected to high-temperature holds for 1 – 1000 h at 1050 – 1300°C in the furnace (air) atmosphere.

The structure and the phase and chemical compositions of the structural components of the protective coatings and of the alloy were studied using a Neophot-32 light microscope with an attached computer and a Phillips SEM 535 scanning electron microscope with a EDAX Genesis 2000 attachment for microanalysis.

The electron microscope studies were performed by the method of diffraction electron microscopy of thin foils using an EMV 100L microscope. The foils were prepared by the method described in [10].

RESULTS AND DISCUSSION

In the initial condition the external zone of the complex coating consists of a NiAl chromium-alloyed β-phase bearing 20 wt.% Al (layer *1* in Fig. 1). The internal layer of the coating consists of a mixture of alloyed β-, γ′- and γ-phases (layer *2* in Fig. 1). An alloyed β-phase is located on the boundary with the diffusion zone of the CrAl GCC (layer *3* in Fig. 1) and contains 18 – 20 wt.% Al. The refractory elements of the alloy (W, Re, Mo) do not diffuse into the complex coating. The total thickness of the coating is 80 – 90 μm.

A diffusion zone with dispersed segregations (layer *4* in Fig. 1), which is enriched with Co, Re, W, and Cr, forms on the interface of the coating and the ZhS36-VI alloy.The matrix of the diffusion zone is a β-phase with reduced content of Al. A high concentration gradient with respect to Ni, Al, Cr, W, Re forms on the alloy-coating interface. Thus, the deposition of a CrAl GCC onto alloy ZhS36-VI causes growth in the total content of chromium in the coating after the gas aluminizing, which is especially significant in the diffusion zone. The presence of chromium in the external zone containing a (Ni, Co)Al β-phase matches approximately its dissolution in the β-phase at the temperatures used. Under the diffusion zone alloy ZhS36-VI acquires a thin altered zone with a matrix represented by a Ni_3Al γ′-phase (layer *5* in Fig. 1).

High-temperature holds at 1050 – 1300°C for 1 – 1000 h destroy the layered structure of the complex coating (Figs. 2 and 3). The external zone undergoes a $\beta \rightarrow \gamma'$ decomposition but preserves a high content of a NiAl β-phase containing 16 – 17 wt.% Al. It also contains a layer of an alloyed Ni_3Al γ′-phase and intermediate layers of a mixture of $\gamma + \gamma'$ phases with fine dispersed segregations.

The gradient of aluminum concentration on the boundaries of the CrAl GCC + Ni – Cr – Al – Ta – Re – Y IPC + Al – Cr – Ni – Y IPC stabilizes the structural and phase state of the complex coating. Alloying of the internal layer of the Ni – Cr – Al – Y system with such elements as Re and Ta raises considerably its structural stability due to the lowering of the diffusion permeability. In accordance with the data of [4] tantalum dissolves virtually fully in the γ′-phase; rhenium is virtually insoluble in the β- and γ′-phases and is concentrated in the β-phase. All this factors should raise the protective properties of the coating at high temperatures.

Figure 3 presents the microstructure of the protective coating after a 200-h hold at 1150°C. It can be seen that the

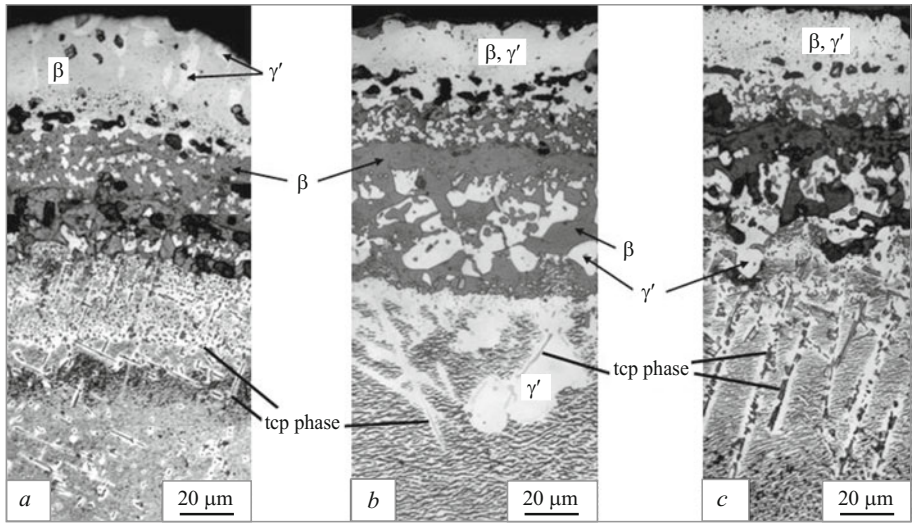
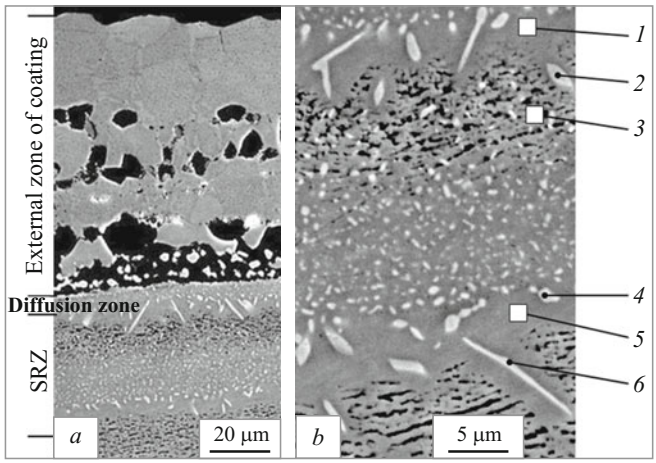


Fig. 2. Microstructure of a complex coating of CrAl GCC + Ni – Cr – Al – Ta – Re – Y IPC + Al – Ni – Cr – Y IPC on alloy ZhS36-VI after a hold at 1100°C for 100 h (*a*), 500 h (*b*) and 1000 h (*c*). × 500.

coating consists of an external zone, remnants of the diffusion zone and a secondary reaction zone (Fig. 3*a*). The SRZ grows from the diffusion zone of the coating with a coarse γ′-phase matrix containing secondary phases enriched with W, Re, Mo, and Cr (Fig. 3*b* and *c*). These phases are represented by a μ-phase of type $(Ni, Co)_7(Cr, W, Re, Mo)_6$ [1], and we can observe a transition from an acicular (plate) shape to a round shape of tcp phases in the SRZ in the direction from the matrix to the coating. The high-temperature tests increase the thickness of the SRZ, the growth of which at a constant temperature obeys a parabolic dependence and reflects the diffusion nature of the formation of this zone. The mentioned structural changes in the "alloy – protective coating" system are observed in the temperature range of 1050 – 1200°C. At a temperature exceeding 1200°C a SRZ does not form under the coating. We observe intense coagulation and growth of tcp phases in the diffusion zone of the coating. The external zone of the coating undergoes the following phase transformations: β-NiAl → γ′-Ni_3Al → γ-solid solution.

Thus, the structural transformations on the interface of alloy ZhS36-VI with γ/γ′ structure, where the β-phase is supersaturated with refractory elements, and the diffusion zone of the coating with matrix represented by a β-NiAl phase, cause the appearance and growth of SRZ in high-temperature holds. The diffusion processes on the interface transform the structure of the alloy into a more stable three-phase structure of a γ – γ′ – tcp phase. Later on, these three phases grow together, and the interface with the SRZ shifts into the alloy providing accelerated diffusion exchange for its further growth. The wavy behavior of the front of the growth of the SRZ/alloy interface is connected with segregation inhomogeneity of the alloy in dendrite arms and in the arm spacing.

To obtain exhaustive data on the effect of high-temperature holds on the structure and phase composition of a complex coating of CrAl GCC + Ni – Cr – Al – Ta – Re – Y IPC + Al – Ni – Cr – Y IPC and on the reaction zone of its interaction with the substrate metal (single-crystal alloy ZhS36-VI) we resorted to the method of transmission electron microscopy of thin foils and performed phase identification of the arising dispersed phases and determined the morphology and crystallographic features of the processes of their formation and growth.



c

Region*	Content of elements in the layer, wt.%									
	Al	Ti	Cr	Co	Mo	W	Re	Nb	Ta	Ni
1	9.0	1.0	4.4	5.0	0.7	4.3	0.9	1.3	1.5	Matrix
2	1.4	0.3	11.1	5.8	3.0	45.0	12.0	0.8	–	20.0
3	8.8	0.8	4.5	4.9	0.9	5.5	0.6	1.3	2.0	Matrix
4	1.2	0.3	9.8	7.1	4.5	44.5	11.5	0.8	–	20.0
5	9.0	1.5	3.9	6.3	1.0	3.8	0.8	1.4	0.3	Matrix
6	2.2	0.6	7.9	7.4	3.0	41.0	10.9	0.9	–	26.0

* See Fig. 3*b*.

Fig. 3. Microstructure of a complex coating (*a*), a SRZ under the coating (*b*), and its chemical composition (*c*) after a hold at 1150°C for 200 h: *1*, *3*, *5*) γ′-phase; *2*, *4*, *6*) tcp phase.

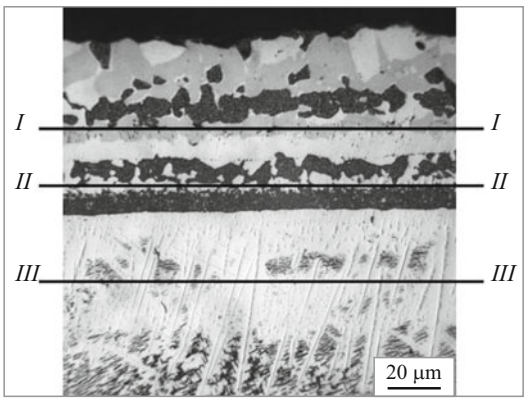


Fig. 4. Scheme of cutting of specimens with coating for electron microscope transmission studies: *I – I*, *II – II*, *III – III*) sections for preparation of foils.

The thin foils for the transmission electron microscope studies were cut in parallel to the surface of a coated specimen. The first foil was cut at a distance $h \le 50$ μm from the surface of the coated specimen (section *I – I* in Fig. 4), the second foil was cut at a distance $h \sim 70$ μm (section *II – II* in Fig. 4), the third foil was cut a $h = 90 – 100$ μm, which corresponded to about the middle of the alloy-coating transition zone (section *III – III* in Fig. 4), and the fourth foil was cut at $h = 1$ mm, i.e., from the substrate metal.

The external zone of the coating contains a layer of alloyed γ′-phase and small layers of γ′-phase with fine dispersed segregations (Fig. 5). The electron diffraction pattern corresponds to zone [100] and proves preservation of the crystallographic orientation and "single-crystal nature" of the alloy in the given layer of the coating.

At a distance $h \le 50$ μm from the surface (Fig. 5*a* and *b*) the external zone of the coating contains no segregation of a μ-phase or any other phases; the structure is represented by a γ′-phase with different morphology (a homogeneous γ'_1-phase with subgrain boundaries and a considerable content of dislocations, a mixture of $(\gamma + \gamma'_2)$-phases consisting of a cuboid $(\gamma + \gamma'_2$-phase and thin layers of γ-phase).

The fine structure of the external zone of the coating near the transition zone ($h \sim 70$ μm) is characterized by the following features (Fig. 5*c*). The structure contains a considerable number of bulky spherical segregations of a μ-phase, the majority of which bear flat internal defects in the basal plane of the crystal lattice. The segregations of the μ-phase are distributed in the structure not uniformly, i.e., in some regions the particles are accumulated and some bear individual inclusions. The content of the μ-phase particles decreases with decrease in the distance to the external surface of the coating and their diameter fluctuates within 0.5 – 2 μm (the mean value is about 1 μm). The γ′-phase surrounding the spherical particles of the μ-phase exhibits no "cuboid" morphology, presence of low-angle subgrain boundaries, dislocations with low density, and dislocation clusters on subgrain boundaries, as well as single annealed γ-twins.

The reaction zone situated under the complex coating contains extended acicular segregations. Typical structures

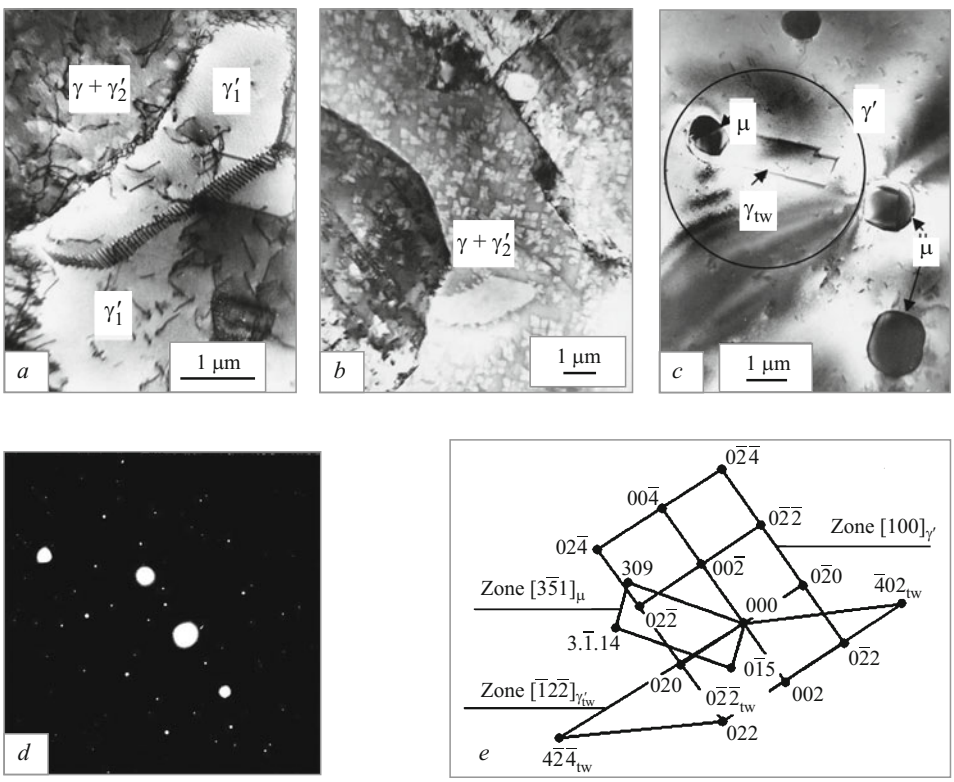


Fig. 5. Fine structure of the external zone of a complex coating after a hold at 1100°C for 500 h: *a*, *b*) near the surface (section *I – I* in Fig. 4); *c*) at the coating-alloy transition zone (section *II – II* in Fig. 4); *d*, *e*) microdiffraction from the encircled region in Fig. 5*c* and diagram of its deciphering respectively.

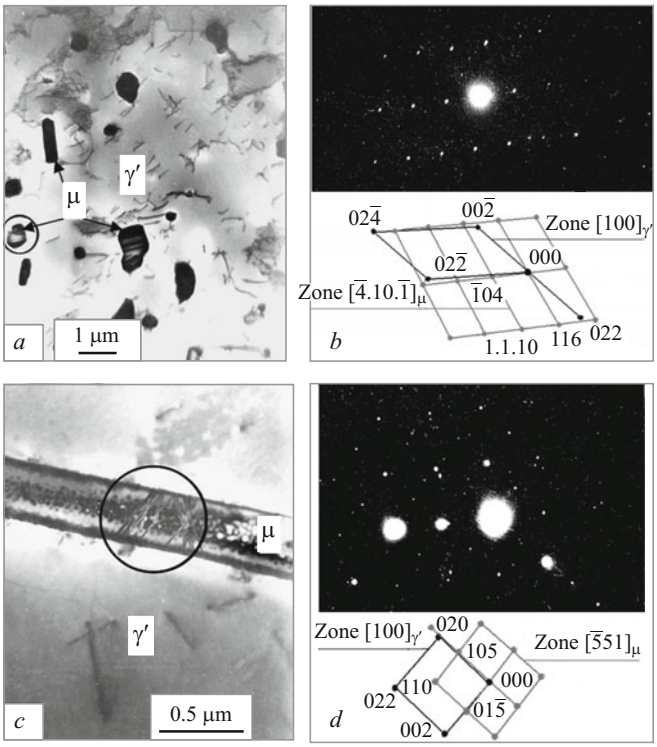


Fig. 6. Fine structure of the reaction zone of interaction between the complex coating and single-crystal alloy ZhS36-VI after a 500-h hold at 1100°C (section III – III in Fig. 4): *a*) round-shape tcp phase against the background of homogeneous γ′-phase; *b*) microdiffraction from the region in Fig. 6*a* and diagram of its deciphering; *c*, *d*) plate-shape tcp phase against the background of a homogeneous γ′-phase and microdiffraction from the encircled region with diagram of its deciphering.

of the reaction zone discovered by the electron microscope analysis are presented in Fig. 6. Particles of segregations of different shapes and sizes distributed nonuniformly in the studied regions of the reaction zone are observable against the background of a homogeneous γ′-phase (Ni_3Al). According to the data of the microscopic diffraction analysis all these particles are segregations of a tcp β-phase, and the parameters of their crystal lattice are close to those of Co_7Mo_6. The μ-phase segregations are of two morphological types, i.e., round (Fig. 6*a*) and plate (Fig. 6*c*) ones. Transition from the plate morphology to the equiaxed one occurs in the direction from the substrate metal to the surface of the coating specimen. The plates of the μ-phase have a habit of $\{111\}_{\gamma'} // (001)_{\mu}$, and the lattices of the μ- and γ′-phases obey a strict crystallographic orientation relation (OR) of one of the following two types: $(001)_{\mu} // \{111\}_{\gamma'}$, $\langle 100\rangle_{\mu} // (01\text{-}1)_{\gamma'}$ (type CR1) or $(001)_{\mu} // \{111\}_{\gamma'}$, $\langle 100\rangle_{\mu} // (11\text{-}2)_{\gamma'}$ (type CR2) [11]. The morphological and crystallographic characteristics of the plates of the μ-phase reflect their nucleation and growth in the γ′-phase. The morphological and crystallographic features of the μ-phase are a result of its bonding to the β-phase of the initial chromium-aluminide coating. The crystal lattices of the β- and μ-phases obey a strict crystallographic relation of type CR1. This is responsible for the specific orientation relation of type CR3, i.e., γ′/μ equiaxed after the $\beta \rightarrow \gamma'$ transformation due to the high-temperature hold. The observed scattering of the CR3 γ′/μ-equiaxed is caused by the intense diffusion processes occurring under the long-term high-temperature hold.

The structural changes in alloy ZhS36-VI [100] near the transition zone at a distance of 1 mm from the surface of a coated specimen are presented in Fig. 7. It can be seen that the particles of the γ′-phase have changed considerably their usual cuboid shape and have stretched in directions $[100]_{\gamma}$. This zone contains no segregation of other phases. Such a structure is formed in the alloy after high-temperature holds due to redistribution of alloying elements in the matrix (γ-phase) and enrichment of the faces of the cuboid γ′-phase with the γ′-forming elements of the alloy [4, 7].

CONCLUSIONS

1. After a 1 – 1000-h hold at a temperature of 1050 – 1300°C the structure of the complex coating of CrAl GCC + Ni – Cr – Al – Ta – Re – Y IPC + Al – Ni – Cr – Y IPC on alloy ZhS36-VI undergoes considerable changes; however, the high-content of a NiAl β-phase bearing 16 wt.% Al is preserved in the external layer of the coating and provides high protective properties.

2. The structural transformations on the "diffusion zone of the coating – substrate metal" interface cause the appearance of a secondary reaction zone (SRZ) in alloy ZhS36-VI,

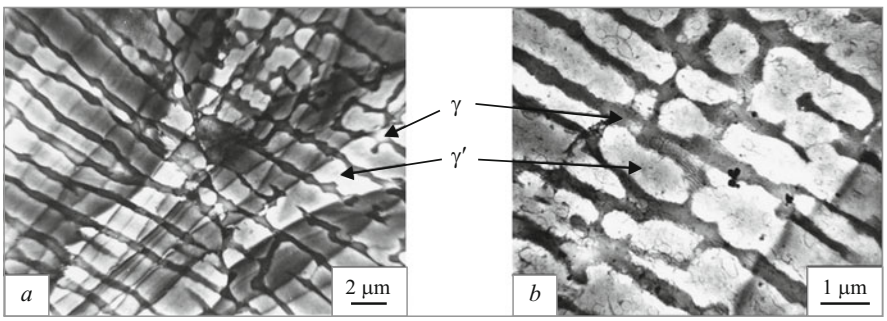


Fig. 7. Fine structure of the alloy near transition zone after a 500-h hold at 1100°C: *a*) low-angle boundary; *b*) (γ + γ′)-structure.

which grows due to high-temperature holds. This yields a steady $\gamma - \gamma' -$ tcp three-phase structure. The tcp phases are μ-phases of different morphology enriched with refractory elements (W, Re, Mo, Cr). The chemical composition of the μ-phases depends on the temperature of the hold, and the transition from a plate morphology to an equiaxed one occurs in the direction from the substrate metal to the surface of the coated specimen.

3. After a high-temperature hold the internal layer of the Ni – Cr – Al – Ta – Re – Y IPC acquires numerous spherical segregations of a μ-phase the content of which decreases upon shortening of the distance to the external surface of the complex coating. Bulky spherical segregations of μ-phases 0.5 – 2 μm in diameter are located in a coarse γ'-phase that has lost its cuboid shape.

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